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(54) Method of producing a sinterable lithium orthosilicate Li_4SiO_4 powder

(57) A method of producing a sinterable lithium orthosilicate (Li_4SiO_4) powder having a phase purity of more than 95% comprises

a) producing an aqueous lithium hydroxide solution;

b) introducing amorphous SiO_2 into the solution formed from step a)—thereby forming a suspension—and adding H_2O_2 to said suspension;

c) spray-drying the suspension formed from step b) to form a powdery/pulverulent dry residue; and

d) heating the dry residue formed from step c) for reaction and calcination at a temperature in the range of from 500°C to 1000°C.

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SPECIFICATION

Method f producing a sinterable lithium orthosilicate Li_4SiO_4 powder

The invention relates to a method of producing a sinterable lithium orthosilicate Li_2SiO_4 powder having a phase purity of more than 95%.

It has already been proposed to use lithium-containing, oxidic ceramics materials—lithium orthosilicate, for example—as breeder materials for fusion reactors to obtain tritium. In most of the cases for producing Li_4SiO_4, solid Li_2CO_3 and SiO_2 powders were finely ground and mixed, and such mixtures were subjected to heat-treatment either when they were in their dry state or when they were in the form of sludges to be dried, said heat-treatment including drying and calcining or melting at high temperatures. Temperatures of 700°C and more were used for these heat-treatment processes which, in the main, were of a long duration (between twenty hours and two days). If, after cooling, the particle size was in the range of from 30 μm to 10 μm, the particles had to be ground for between eight and forty-eight hours in order to obtain the desired size.

Impurities may result from the grinding and pulverising of not only the starting substances, but also the calcined reaction product. In addition, these solids reactions generally only account for between 90% and 95% of the desired phase in the end product.

The invention seeks to provide a simple method of producing Li_4SiO_4, so that the impurities in the end product can be eliminated and so that the considerable amount of time and energy needed for the prior art methods can be reduced. The grinding and lengthy diffusion-annealing steps at temperatures higher than 700°C should also be eliminated.

According to the invention, the object is achieved by the following procedural steps:

a) producing an aqueous lithium hydroxide solution;

b) introducing amorphous SiO_2 into the solution formed from step a)—thereby forming a suspension—and adding H_2O_2 to said suspension;

c) spray-drying the suspension formed from step b) to form a powdery dry residue; and

d) heating the dry residue formed from step c) for reaction and calcination at a temperature in the range of from 500°C to 1000°C.

The following reaction takes place in the lithium hydroxide solution:

$$4LiOH + aq + SiO_2\ (\text{amorphous}) + H_2O_2 \rightleftharpoons Li_2SiO_3.xH_2O + Li_2O_2 + aq + H_2O_2.$$

The addition of H_2O_2 is important for the quality of the powder which results after heat-treatment because, if H_2O_2 is not present, the powder sticks or coalesces during calcination. After the spray-drying process, a powdery or pulverulent dry residue is obtained which is composed of the stoichiometric mixture of $Li_2SiO_3.xH_2O$ and Li_2O_2. Because the subsequent heating of the dry residue, the powder mixture reacts to form Li_4SiO_4. Reaction and calcination are preferably effected at 600°C for a period of approximately two hours. The product of the method is composed of small, disintegrated spheres having a particle size of from approximately 2 μm to 6 μm. The powder is highly sinterable. Densities higher than 90% of the theoretical density are achieved during the sintering process.

Because of its high degree of purity and its high molecular lithium density, the lithium orthosilicate produced in accordance with the method of the invention is particularly well-suited for use as a breeder material for fusion reactors to obtain tritium.

The invention is explained more fully hereinafter with reference to one operational example.

Example:

In accordance with the reaction equation:

$$4LiOH + SiO_2 + aq + H_2O_2 \rightarrow Li_2SiO_3.xH_2O + Li_2O_2 + aq,$$

an aqueous suspension of amorphous SiO_2 (AEROSIL produced by DEGUSSA) was introduced into an aqueous solution of lithium hydroxide with constant stirring, and lithium metasilicate was initially formed within approximately one hour.

In order to improve the subsequent calcination of the dried powder, the surplus LiOH was reacted immediately prior to the spray-drying process in suspension with H_2O_2 (in excess) to form Li_2O_2.

Table: Deposits for spray-drying lithium orthosilicate

No.	in solution:		as suspension:			
	LiOH (g)	H_2O (cm³)	SiO_2 (g)	H_2O (cm³)	Li_2SiO_3/Li_2O_2 (g/l)	Number of Deposits
1	63.87	750	40.06	250	~90	2

The suspension was spray-dried at from 250°C to 350°C, respectively. The yield was more than 90%. By air-treating the lithium hydroxide solutions and the suspensions, the powders contained up to 6% by weight of carbonate components which were removed during the calcining step.

It was possible to calcine the spray-dried, stoichiometric powder mixture at from 500°C to 600°C. By converting the surplus lithium hydroxide into Li_2O_2, the possibility of melting occurring here (T_M(LiOH) = 450°C) is almost entirely eliminated.

After the powder had been calcined, it could be compressed up to >90% of the theoretical density by being pressed and sintered at 1100°C for six hours. The sintered samples always produced mono-phase Li_4SiO_4.

CLAIMS

1. A method of producing a sinterable lithium orthosilicate Li_4SiO_4 powder having a phase purity of more than 95%, characterised by the following procedural steps:
a) producing an aqueous lithium hydroxide solution;
b) introducing amorphous SiO_2 into the solution formed from step a)—thereby forming a suspension—and adding H_2O_2 to said suspension;
c) spray-drying the suspension formed from step b) to form a powdery dry residue; and
d) heating the dry residue formed from step c) for reaction and calcination at a temperature in the range of from 500°C to 1000°C.

2. A method as claimed in claim 1, in which the dry residue is heated at a temperature of 600°C.

3. A method of producing a sinterable lithium orthosilicate Li_4SiO_4 powder having a phase purity of more than 95%, as claimed in claim 1 or 2, substantially as hereinbefore described and exemplified.

4. A breeder material for a fusion reactor for producing tritium, comprising sinterable, pure Li_4SiO_4 powder produced in accordance with the method as claimed in claim 1, 2 or 3.

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